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AIR RESOURCES BRANCH
ATMOSPHERIC RESEARCH AND
SPECIAL PROGRAMS SECTION

ESTIMATION OF ATMOSPHERIC CONCENTRATIONS
IN THE VICINITY OF EVAPORATING PCB SPILLS

ARB-22-82-ARSP

A Report Prepared for
Ministry of the Environment
Air Resources Branch

by

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and Applied Chemistry
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SUMMARY

A mathematical model is derived which enables evaporation rates to be calculated for spills of liquids, such as PCBs, of low to moderate volatility, and permits estimation of atmospheric concentrations of the volatilizing substance at points in the vicinity of the spill site. The model is fitted to data obtained from the vicinity of a site contaminated by PCBs. The model is also applied for illustrative purposes to an actual PCB spill. A simple calculation procedure is defined which can be used for on-site estimation of exposure hazard to evaporating substances.

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1. INTRODUCTION

When a chemical substance is spilled on land, evaporation may be a significant mechanism of mass loss. A knowledge of the evaporation rate is useful in several respects. For volatile liquids (such as gasoline) it will determine the "lifetime" of the spill. For flammable substances it will influence the extent of fire hazard in the vicinity. For toxic substances it will influence the dimensions of the zone in which it is necessary to take protective measures to avoid excessive exposure.

It is thus valuable to have the capability of calculating, at the spill site, the rate of evaporation and the likely atmospheric concentrations at various points in the vicinity. A desirable feature of such a capability is that the calculation can be done on-site, by the personnel involved, without the need to use sophisticated computer programs or have access to advice from others. In this work we devise and use such a calculation procedure in the full expectation that it will be subject to future improvement. The primary aim is to establish the framework for a reasonably simple procedure which is based on physically reasonable assumptions.

It is assumed that the person undertaking the calculation has available the following information:

- (i) chemical identity of the spilled substance.
- (ii) the substance's vapour pressure or at least its boiling point.
- (iii) the dimensions of the spill (area, volume and thickness or depth)
- (iv) ambient meteorological conditions of temperature, wind speed and direction.
- (v) knowledge of the terrain topography.

For interpreting the results of the calculation it may be useful also to have information on acceptable exposure concentrations, eg. TLVs or flammability limits.

The approach taken is to devise in Section 2 a mathematical model of the evaporation and dispersion process. In Section 3 this model is fitted to experimental data obtained from a site in Ontario in which there had been a spillage of polychlorinated biphenyls (PCBs). In Section 4 the model is applied to a second case in which a quantity of PCBs was spilled in a school yard as a result of transformer failure and in which air concentration data were also obtained. Some conclusions and recommendations and discussion of limitations are given in Section 5. A draft "manual" is included in Appendix I for undertaking the calculation.

2. MATHEMATICAL MODEL

2.1 Approach and Limitations

In this section we first address the question of calculating the evaporation rate of a spill. This is followed by derivation of a plume dispersion model. The two are then linked. This linkage is simple when the substance is fairly involatile and the concentrations achieved over the pool are well below the saturation values. The rate of evaporation is then little affected by the concentration in the overlying air and the evaporation rate is kinetically controlled. In cases when the plume is advected only slowly from the pool there may be "blanketing" and the atmospheric concentration reduces the evaporation rate. Finally there is a brief review of vapour pressure determinations for liquids in general but for PCBs in particular.

It is assumed that the pool temperature is known. This will generally be close to ambient air temperature but there may be evaporative cooling and heating by solar radiation; thus, some judgement is necessary to include these effects.

If the liquid is absorbed into a porous substrate such as soil, the absorbed liquid is shielded from evaporation and evaporation will be retarded. This effect is not included in this work; although methods of addressing the issue are discussed later.

Throughout this work SI units are used, but conversion factors are given in Appendix I.

2.2 Evaporation Rate

When a quantity of liquid is spilled on the ground, it rapidly achieves environmental temperatures and becomes subject to spreading, evaporation, and penetration into the underlying ground. If the surface is water-logged, there will be relatively little penetration

but spreading will be enhanced.

If a volume $V \text{ m}^3$ is spilled over an area $A \text{ m}^2$, the depth is D or $V/A \text{ m}$. It will evaporate at a rate controlled by the liquid's vapour pressure P (Pa) (as influenced by temperature) and composition (mole fraction x) and the evaporation mass transfer coefficient K_e , which generally has a value of approximately 10^{-2} m/s at normal wind speeds (Mackay and Matsugu, 1973). Specifically the rate of evaporation $Q \text{ g/s}$ will be

$$Q = K_e A P x M / (RT)$$

where R is the gas content ($8.314 \text{ Pa m}^3/\text{mol K}$), T is absolute temperature (K) and M is the molecular weight (g/mol).

A convenient expression for K_e is a simplification of that devised by Mackay and Matsugu (1973); namely,

$$K_e = 0.0025 U^{0.78}$$

where U is the wind speed (m/s).

In many cases the liquid is pure; thus, the mole fraction term x is unity and can be ignored.

In an askarel (PCB transformer oil), x is in the range 0.5 to 0.75. In practice, it is acceptable to interpret x as the volume fraction of the substance of interest.

The equation for Q is useful in two respects. First, it gives the source strength of the spill which is used later in the dispersion calculation. Second, it can be used to estimate the spill lifetime τ . Evaporation will be complete when $Q\tau$ equals the mass in the spill (g), ie. $10^6 V d$ where d is the liquid density (g/cm^3), there being 10^6 cm^3 in a m^3 . It follows that

$$\begin{aligned} \tau &= 10^6 V d / Q \text{ seconds} \\ &= 10^6 V d / [K_e A P x M / (RT)] \\ &= 10^6 D d RT / (K_e P x M) \end{aligned}$$

where D is depth, ie. V/A.

Typically d is 1.0, T is 288K, K_e is 0.01 m/s, x is 1.0 and M is 200 g/mol; thus,

$$\begin{aligned}\tau &\approx 1.2 \times 10^9 D/P \text{ seconds} \\ &\approx 3.3 \times 10^5 D/P \text{ hours.}\end{aligned}$$

For a 1 mm. thick spill ($D=10^{-3}$ m) of a volatile liquid of vapour pressure 10^3 Pa ie. 0.01 atm or 7.6 mm Hg, τ is thus 0.33 hours or 20 minutes.

2.3 Plume Dispersion

Assuming that a constant source strength or a concentration immediately above the evaporating pool is known and is independent of the atmospheric dispersion processes, it is possible to calculate the concentration at points downwind if certain assumptions are made concerning

- (1) steady state vs. unsteady state (time variance)
- (2) wind speed and direction constancy with time and position
and as influenced by pool and adjacent terrain roughness
- (3) diffusivity constancy with time and position in three
dimensions
- (4) interaction of the substance with the ground (ie. reflection
or absorption)
- (5) buoyancy effects of the substance at high concentration

In general, different models arise from different assumptions being applied, the more severe the assumptions, the simpler the model.

In this work, we reviewed dispersion models, particularly the conventional models reviewed by Turner (1970) and the vapour cloud dispersion model described by Reijnhart et al. (1980). The latter model is very effective but unfortunately does not lead to a simple expression for concentration or mass flux. Accordingly, we have derived a novel model which is essentially an adaptation of the Gaussian model, which it is hoped will adequately describe the concentration profiles. It is derived here from first principles.

If a point source is emitting substance at Q g/s into a wind of velocity U m/s and the plume spreads horizontally to width H and vertically to width h , there being homogeneous concentrations (C g/m³) within these dimensions it follows that the conservation of mass

requires that

$$Q = CUHh \quad (1)$$

$$\text{thus } C = Q/UHh \quad (2)$$

In practice C is not constant but varies in a near-Gaussian manner in both dimensions. Postulating that

$$C = C_0 \exp(-y^2/2\sigma_y^2 - z^2/2\sigma_z^2) \quad (3)$$

where C_0 is the centreline concentration gives the concentration at any width y or height z . Conservation of mass requires that the integrated concentration equals Q , y being integrated from $-\infty$ to $+\infty$ and z from 0 to $+\infty$ (if there is total reflection from the ground). Now

$$\int_{-\infty}^{+\infty} \exp(-y^2/2\sigma_y^2) dy = \sigma_y \sqrt{2\pi} \quad (4)$$

$$\int_0^{\infty} \exp(-z^2/2\sigma_z^2) dz = \sigma_z \sqrt{2\pi}/2 \quad (5)$$

$$Q = C_0 U (\sigma_y \sqrt{2\pi}) (\sigma_z \sqrt{2\pi}/2) \quad (6)$$

$$\text{or } C = (Q/U\pi\sigma_y\sigma_z) \exp(-y^2/2\sigma_y^2 - z^2/2\sigma_z^2) \quad (7)$$

which is the conventional ground level emission equation.

We are concerned with concentrations around the pool; thus we redefine y as the perimeter distance rather than the normal distance as shown in Figure 2.1. It follows that y can be derived now from an angle and the radius rather than a distance. The total perimeter at a radius X is $2\pi X$ and is equivalent to 360° ; thus, if θ

is the angle between the point of interest and the wind direction

$$y = \theta 2\pi X / 360$$

Alternatively if θ is expressed in radians ϕ

$$y = \phi X$$

We also redefine σ_y in terms of an angle σ_θ as

$$\sigma_y = \sigma_\theta 2\pi X / 360 \quad \text{or} \quad \phi X$$

Inserting these into the Gaussian equation gives

$$C = Q(\pi U \sigma_z (\sigma_\theta 2\pi X / 360)) \exp(-\theta^2 / 2\sigma_\theta^2 - z^2 / 2\sigma_z^2)$$

or

$$C = 180Q / (\pi^2 U \sigma_z \sigma_\theta X) \exp(-\theta^2 / 2\sigma_\theta^2 - z^2 / 2\sigma_z^2) \quad (8)$$

If σ_θ becomes large there will be some "wraparound", ie. the substance will diffuse over 180° and will "double up" the concentration. In practice this does not occur appreciably if σ_θ is less than 60° . It can be included by replacing

$$\exp(-\theta^2 / 2\sigma_\theta^2) \quad \text{by} \quad \exp(-\theta^2 / 2\sigma_\theta^2) + \exp(-(\theta - 360)^2 / 2\sigma_\theta^2)$$

This is similar in principle to the hypothetical "second stack" used to predict reflected concentrations. Effectively it doubles concentrations at 180° . In principle a $(\theta - 720)$ term could also be included but this is necessary only if σ_θ exceeds 180° . In practice (as is shown later) if σ_θ is 180° the concentration varies only by some 10% around the perimeter. There is thus no merit in using values greater than 180° .

These concentrations are illustrated in Figure 2.I. It is concluded that the difference in concentration around the perimeter is adequately expressed by the equation below provided that only values of σ_θ less than 180° are used.

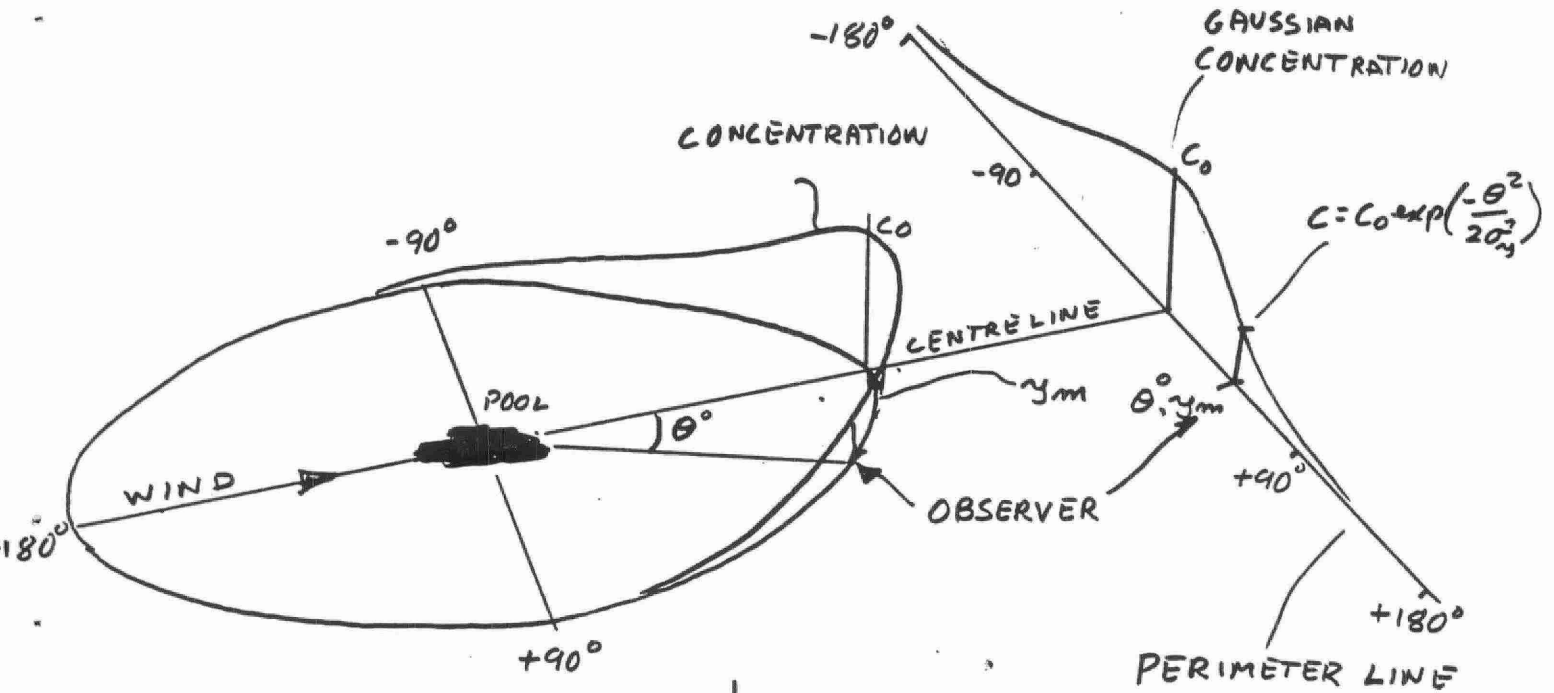
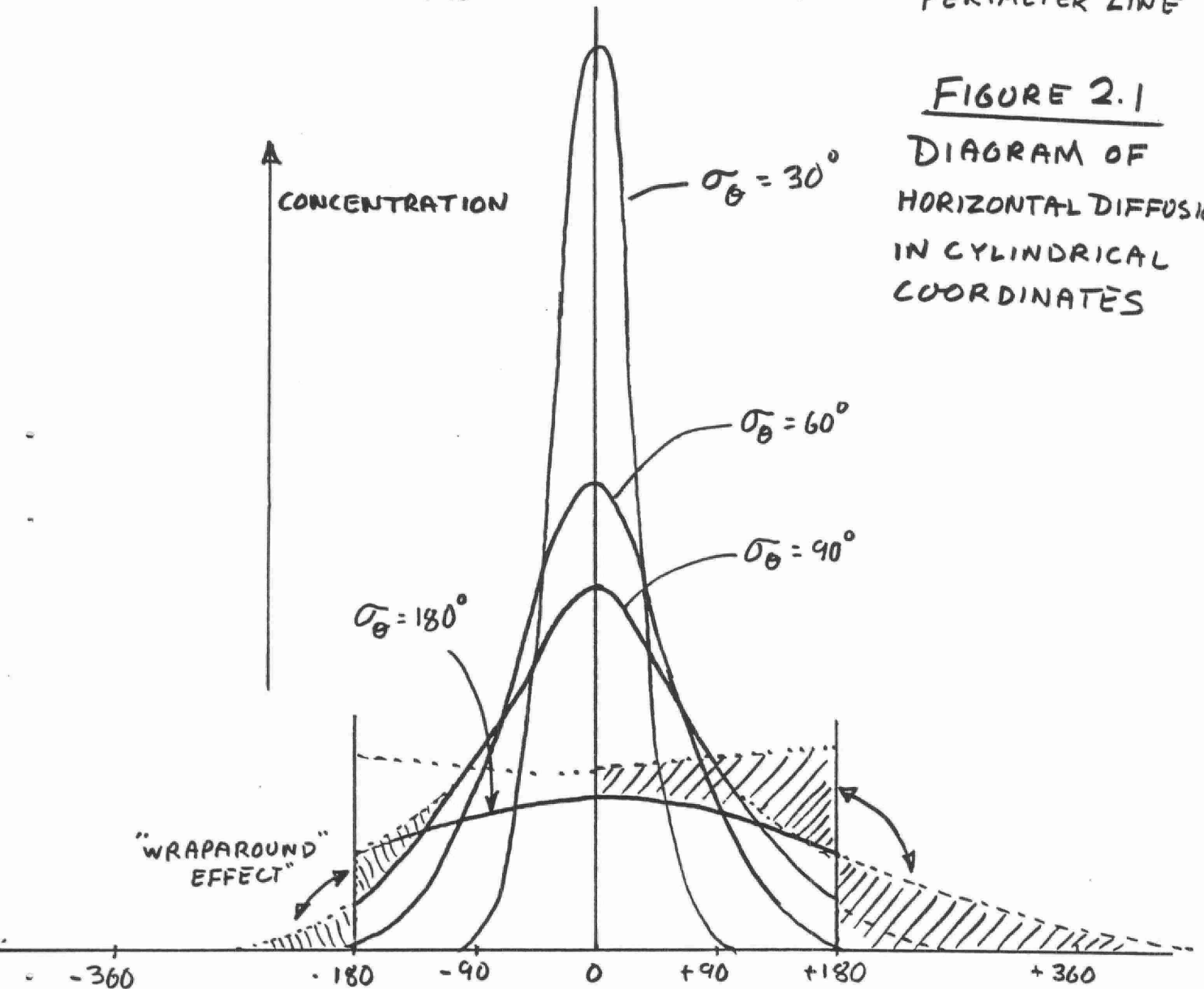


FIGURE 2.1
 DIAGRAM OF
 HORIZONTAL DIFFUSION
 IN CYLINDRICAL
 COORDINATES



As is shown later, when θ is 180° the concentration at 180° is actually slightly greater than the concentration at 0° , which is, of course, physically unrealistic. This slight discrepancy can be readily avoided by setting a maximum value of 160° for θ at which angle the radial distribution is quite even.

$$C = 180Q/(\pi^2 U \sigma_z \sigma_\theta X) \exp(-z^2/2\sigma_z^2) [\exp(-\theta^2/2\sigma_\theta^2) + \exp(-(\theta-360)^2/2\sigma_\theta^2)] \quad (9)$$

If desired, the angular dispersion quantities σ_θ and θ can be replaced by the perimeter distances σ_y and y . This may be advantageous because it avoids any confusion between degrees and radians during calculation. Unfortunately, it is convenient to measure wind direction relative to the point of interest as an angle. Considering these issues has led to a compromise in which σ_y is calculated and included in the equation, but σ_θ is also calculated from it. The calculation sequence is given later in the Appendix.

The centreline ground level concentration at $\theta = 0$, $Z = 0$ becomes from Equation 9

$$C = Q/(\pi U \sigma_z \sigma_y) \exp(-z^2/2\sigma_z^2) [\exp(-\theta^2/2\sigma_\theta^2) + \exp(-(\theta-360)^2/2\sigma_\theta^2)] \quad (10)$$

The concentration $(Q/\pi U \sigma_z \sigma_y)$ is approximately the centreline ground level concentration. The actual value is slightly higher because of the term including $(\theta - 360)$ which is not zero when θ is zero. When σ_θ is 130° , i.e. the "worst case", the difference is only 14%.

It can be shown that this equation reduces essentially to Equation 2 under certain conditions. If a non-Gaussian expression is used for the vertical concentration, the concentration being assumed to be constant to height h, then

$$Q = C_o U \sigma_y \sqrt{2\pi} h$$

or $C_o = Q / \sqrt{2\pi} U \sigma_y h$ i.e. h replaces $\sigma_z \sqrt{2\pi} / 2$

which leads to

$$C = 180Q / \pi^2 U \sigma_\theta X \sqrt{2/\pi} h [\exp(-\theta^2 / 2\sigma_\theta^2) + \exp(-(\theta-360)^2 / 2\sigma_\theta^2)]$$

When σ_θ is 180° , the exponential terms on the right assume the following values for selected values of θ :

$$\begin{aligned} \theta = 0^\circ & , \quad 1 + 0.135 = 1.135 \\ \theta = 45^\circ & , \quad .969 + 0.216 = 1.185 \\ \theta = 90^\circ & , \quad .882 + .325 = 1.207 \\ \theta = 135 & , \quad .755 + .458 = 1.213 \\ \theta = 180 & , \quad .607 + .607 = 1.214 \end{aligned}$$

The mean value is 1.191 and the maximum variation is only 0.056 or 4.7%.

The radial distance X is related to the perimeter H as $H = 2\pi X$.

Replacing X with $(H/2\pi)$, the exponential group by 1.191 and σ_θ by 180° gives

$$C = 0.95Q / UHh$$

which is essentially equation (2) derived earlier. It follows that Equation (9) can be expected to give concentrations as a function of radial distance X and height z which are consistent with the mass balance. The equation has been shown to reduce to the intuitively obvious Equation 2.

Correlations for σ_z , σ_θ and σ_y .

The simplest procedure is to assume correlations equations in which σ_z and σ_y increase linearly with distance from the source. Specifically it is proposed that

$$\sigma_z = C_3 H + C_1 X$$

where H is the pool diameter, X is the distance from the pool edge and C_3 and C_1 are constants. Intuitively, C_3 should be small, reflecting the height of plume rise over the pool. When X is zero, σ_z becomes $C_3 H$.

The dispersion coefficient diagrams for σ_z under stability condition C suggest that C_1 is of the order of 0.07 m^{-1} since σ_z rises from 7.5 to 70 m when X increases from 100 to 1000 m. C_1 will also be affected by terrain roughness, trees, buildings, etc. which induce vertical flow. To a first approximation σ_z will be increased by the height of the "object".

It is proposed that

$$\sigma_y = C_4 H + C_2 X/U$$

where U is wind speed; thus, X/U is the diffusion time and C_2 can be viewed as a velocity of spread. When X is zero, σ_y becomes $C_4 H$; thus, C_4 should be of the order of unity. σ_θ is calculated from σ_y as shown earlier.

In the actual pool area ($X = 0$), the concentration thus becomes approximately

$$Q/UC_3 C_4 H^2 \quad \text{g/m}^3$$

which assumes that there is homogeneity of concentrations to a height $C_3 H$ and width $C_4 H$. This will be the highest concentration in the area except in the immediate vicinity of the pool surface where the concentration will be the saturation value of $PM/RT \text{ g/m}^3$.

In practice it will be desirable to express concentrations in ng/m^3 by multiplying by 10^9 or $\mu\text{g/m}^3$ using 10^6 or mg/m^3 using 10^3 .

If parts per million by volume are desired, the concentration in g/m^3 should be multiplied by 10^6 and divided by the substance vapour density at 1 atm. pressure (g/m^3) which is $P_A M/RT$, or at 25°C or 288K , or $42M$ where M is the molecular weight (g/mol).

It is likely that σ_y is dependent on sampling time - which is here 24 hours. For shorter sampling times the plume will be "sharper", σ_y smaller, and local concentrations higher. One could postulate a relationship of the form

$$\sigma_y \propto (\text{sampling time})^n$$

where n may lie in the range 0.3 to 1.0.

2.4 Linking Evaporation and Dispersion

For conceptual purposes, it is convenient to view the evaporation process as occurring as illustrated earlier in Figure 2.1, in which there is a volume of well mixed air overlying the spill. This air is replaced at a rate determined by the wind speed U . If the evaporation rate is Q g/s, then the well mixed concentration above the spill will be $Q/(Uhh)$ g/m³. The saturation concentration immediately at the liquid interface is PM/RT g/m³. The blanketing effect is thus quantified by the ratio of these two concentrations, namely

$$QRT/(UhhPM)$$

But

$$Q = K_e A P M / RT$$

thus the ratio becomes in the case of a pure liquid

$$K_e A / (Uhh)$$

This is the dimensionless ratio of two volumetric flow rates (m³/s), the diffusion or evaporate rate from the interface, and the rate at which the vapour is swept from over the spill. Now A will typically be the same order of magnitude as H^2 ; thus, the ratio becomes $K_e H / (Uh)$. K_e is typically 0.01 m/s, U is 2 m/s (7.3 km/h); thus, the ratio is unity when H/h is 200. The implication is that when the vapour passing over the spill is confined to a vertical height h which is 1/200th of the spill diameter, then there will be blanketing. It is believed that vertical mixing is usually more rapid than this and that typically over a 10m spill the vapour has diffused vertically to of the order of 1m; thus, H/h is 10 and the dimensionless ratio is 0.05 or the evaporation rate is reduced by some 5% due to blanketing. Only in cases where wind speeds are very low, vertical mixing is slow,

and the vapour is negatively bouyant, will blanketing be severe.

From the viewpoint of safety, the worst situation occurs when there is free evaporation and no blanketing; thus, in this work it is best to assume that the evaporation rate is not reduced by this effect. This will generally lead to a slight overestimation of concentration. It is unwise to assume that blanketing increases safety.

2.5 Vapour Pressures

A substance's vapour pressure is a function of temperature alone. Values can be obtained from handbooks such as The Handbook of Chemistry and Physics or The Chemical Engineer's Handbook. Normally, the units reported are atm or mm Hg (torr), which should be converted to Pa

$$1 \text{ atm} = 101325 \text{ Pa}$$

$$1 \text{ mm Hg} = 133 \text{ Pa}$$

If no vapour pressure is available, an estimate can be made from the substance's boiling point T_B (K) using the Clapeyron relation and Trouton's Rule, namely

$$P_E = P_B \exp [10.6 (1 - T_B/T_E)]$$

where P_E is the vapour pressure at environmental temperature T_E (K) and P_B is the vapour pressure of 1 atm or 101325 Pa at the boiling point T_B (K). Note that both temperatures are absolute (ie. °C + 273).

For example, toluene boils at 110°C (383K); thus at 6°C (279K) its estimated vapour pressure is

$$\begin{aligned} & 101325 \exp [10.6(1 - 383/279)] \\ & = 1950 \text{ Pa or } 14.6 \text{ mm Hg.} \end{aligned}$$

The actual value is 10 mm Hg.

This estimation procedure is approximate and tends to over-estimate vapour pressures and thus errs on the side of safety. It is applicable only to liquids, not to solids.

If vapour pressure data P_D is available at a temperature T_D other than environmental conditions, then this equation can also be used, since if it is assumed that

$$P_D = P_B \exp [10.6 (1 - T_B/T_D)]$$

then

$$P_E/P_D = \exp [10.6 T_B (1/T_D - 1/T_E)]$$

For example, the vapour pressure of toluene at 32°C (305K) is 40mm Hg; thus, at 6°C the ratio of vapour pressures is

$$\begin{aligned} P_E/P_D &= \exp [10.6 \times 383 (1/305 - 1/279)] \\ &= 0.29 \end{aligned}$$

thus, P_E is estimated to be 0.29×40 or 11.6 mm Hg (actual value 10mm Hg).

It is preferable to use data as close as possible to environmental temperatures.

As part of this work a literature review was undertaken of PCB vapour pressures. The results are given in Table 2.1, which contains estimates of vapour pressures of PCB isomers and Aroclor mixtures. Full details of the estimation procedure are given in a separate publication (Mackay et al., 1982).

Table 2.1

PCB Vapour Pressures and Boiling Points

Aroclor	Mol Wt. (a)	BP Range °C	Vap. Press. at 25°C (b)	
			atm.	Pa
1016	258	325 - 326	5.3×10^{-7}	.059
1221	192	275 - 320	8.8×10^{-6}	0.89
1232	221	290 - 325	5.3×10^{-6}	0.54
1242	261	325 - 366	$5.3 \times 10^{-7(c)}$	0.054
1248	288	340 - 375	$6.5 \times 10^{-7(c)}$	0.020
1254	327	365 - 390	1.0×10^{-7}	0.010
12-0	372	385 - 420	5.3×10^{-8}	0.005

(a) O. Hutzinger, S. Safe, V. Zitko, The Chemistry of PCB's (CRC press, 1974)

(b) EPA Report 440/4-79-029 , Water Related Environmental Fate of 129 Priority Pollutants 1979.

(c) We believe that these values are suspect. Better values are probably

1242 8.0×10^{-7} atm = 0.08 Pa
 1248 3.0×10^{-7} atm = 0.03 Pa

3. FITTING TO EXPERIMENTAL DATA

The model was fitted to the experimental data provided by the Ministry in the report, "Polychlorinated Biphenyls Survey at Smithville". The approach used was to test various values of the parameters C_1 , C_2 , C_3 and C_4 until a satisfactory fit was obtained. Other forms of correlation were also tested but only the final results are given here. The best values were:

$$C_1 = 0.15 \quad C_2 = 5.0 \quad C_3 = 0.05 \quad C_4 = 1.0$$

When fitting the data, the procedure used was to minimize the error expressed as the absolute value of the logarithm of the ratio of calculated and experimental concentrations. This avoids giving undue weight to high concentration points. The complete set of calculated and experimental data are given in Table 3.1 and illustrated as a function of distance from source X, windspeed U, temperature T and angle θ versus log of concentration ratio in Figures 3.1 to 3.4. These graphs show the dependence of the ratio of calculated and experimental concentrations as a function of each variable. If the correlation was biased, for example, overestimating the effect of distance, this would result in points lying off the horizontal - possibly at an angle. The figures show no such tendency for any variable; thus we conclude the correlation is satisfactory in its treatment of each variable.

It was found that a satisfactory fit at long distances could only be obtained if a constant background concentration of 0.75 ng/m^3 was added to the calculated values.

The exact area of the "spill" was not known in this case; thus, an estimate was made that it was 240 m^2 but not as a single pool. It was regarded as consisting of numerous pools of a total area of 240 m^2 but spread over an area of 7000 m^2 ; thus only 4% of the actual ground area was PCB covered.

It is apparent from the Table and Figures that there is a high inherent variability in the data. This, it is believed, is due

primarily to errors in windspeed and direction, the wind data being measured some distance from the site and averaged over 24 hours.

It was found that 90% of the model estimations were within a factor of 4.0 of the experimental values, which is regarded as fairly successful. It is doubtful if any model can substantially improve the fit of these data.

The value of C_1 of 0.15 is double the "expected" value of 0.07 obtained from dispersion charts. This may be due to ground induced turbulence. For example, there are buildings and trees in the area of height 5 to 10 m; thus it is likely that, at a distance of 100 m, a σ_z increase of only 7 m is too small, the actual indicated increase of 15 m being in reasonable accord with the dimensions of the "objects" and ground undulations.

The value of C_3 of 0.05 is equivalent to 1/20 of the pool diameter. It is important only in the immediate pool area.

C_4 being a coefficient of unity on H can be ignored as a parameter.

C_2 is 5.0 m/s reflecting the "velocity" of increase of the perimeter value of σ_y . Under Class C conditions (6 m/s) between 100 and 1000 m, σ_y increases, according to dispersion charts from 8 to 110 m, i.e. by 102 m. This corresponds to a transit time of 150 s and thus to a horizontal velocity of 0.7 m/s. But this is for a shorter sampling time of typically of 0.5 hours, whereas the present time was 24 hours.

We postulate that σ_y depends on sampling time, the above data suggesting a relationship of the form

$$\begin{aligned}\sigma_y &\propto (\text{sampling time})^{0.5} \\ \text{or } C_2 &= 5.0 (\text{sampling time}/24)^{0.5} \\ &= 1.0 (\text{sampling time})^{0.5}\end{aligned}$$

The "spreading velocity" C_2 for short sampling times is thus 1 m/s which seems physically reasonable.

It must be emphasised that these values are only estimates which must be improved by further determination. The form of the equations also requires validation. In essence, the work is regarded as a step towards a validated procedure.

As a final note, the procedure developed here obtained an estimate of the evaporation rate from the Smithville site of 2.0×10^{-3} g/s.

A copy of the computer program used to generate these results is appended. (Appendix I).

A "calculation manual" was developed and is given in the Appendix. The "manual" was used illustratively for the Isabella Street School incident discussed in the next section.

Table 3.1. Experimental and Calculated Concentrations at Smithville, Ont.

site no.	sample duration (h)	dist from source (m)	θ degrees	wind speed (km/h)	temperature (°C)	concn exptl (ng/m ³)	concn calc. (ng/m ³)
1	24.0	1.0	150.0	9.0	8.0	284.0	124.8
	24.0	1.0	55.0	10.0	13.0	660.0	271.5
	24.0	1.0	160.0	23.0	9.0	50.0	105.4
	24.0	1.0	180.0	17.0	6.0	3.2	87.0
	24.0	1.0	180.0	13.0	4.0	3.7	78.8
	24.0	1.0	120.0	10.0	6.0	177.0	117.0
	24.0	1.0	170.0	13.0	7.0	21.0	77.3
	24.0	1.0	165.0	15.0	3.0	14.9	71.1
	24.0	1.0	110.0	17.0	13.0	410.0	189.1
	24.0	1.0	170.0	16.0	7.0	53.0	96.1
	24.0	1.0	140.0	12.0	11.0	102.0	132.8
	24.0	1.0	30.0	9.0	10.0	395.0	234.5
1	24.0	1.0	65.0	8.0	15.0	1160.0	319.9
	24.0	1.0	85.0	13.0	18.0	935.0	331.6
	24.0	1.0	155.0	20.0	11.0	546.0	128.9
	24.0	1.0	105.0	11.0	13.0	1193.0	213.3
	24.0	1.0	70.0	11.0	11.0	900.0	215.4
	24.0	1.0	125.0	19.0	6.0	29.0	98.7
	24.0	1.0	140.0	12.0	0.0	780.0	130.6
	24.0	1.0	125.0	15.0	13.0	522.0	180.7
	24.0	1.0	165.0	20.0	13.0	115.0	147.1
	24.0	1.0	40.0	12.0	7.0	538.0	170.4
	24.0	1.0	135.0	11.0	9.0	426.0	136.0
AVERAGE CACT=		405.12	AVERAGE CCAL=		159.95		
2	24.0	1.0	120.0	9.0	6.0	89.0	140.7
	24.0	1.0	35.0	10.0	13.0	970.0	287.0
	24.0	1.0	110.0	23.0	9.0	195.0	129.4
	24.0	1.0	20.0	17.0	6.0	258.0	120.4
	24.0	1.0	90.0	13.0	4.0	74.1	108.5
	24.0	1.0	30.0	10.0	6.0	247.0	166.8
	24.0	1.0	100.0	10.0	3.0	52.7	100.9
	24.0	1.0	105.0	15.0	3.0	113.0	90.0
	24.0	1.0	110.0	20.0	7.0	44.0	107.4
	24.0	1.0	160.0	17.0	13.0	65.0	154.3
	24.0	1.0	105.0	16.0	7.0	150.0	125.9
	24.0	1.0	130.0	12.0	11.0	226.0	159.3
2	24.0	1.0	60.0	9.0	10.0	498.0	216.0
	24.0	1.0	155.0	8.0	15.0	184.0	218.3
	24.0	1.0	115.0	20.0	11.0	81.3	152.3
	24.0	1.0	145.0	11.0	13.0	280.0	232.1
	24.0	1.0	160.0	11.0	11.0	23.1	146.6
	24.0	1.0	145.0	19.0	6.0	34.0	90.6
	24.0	1.0	130.0	12.0	9.0	270.0	136.1
	24.0	1.0	145.0	15.0	13.0	100.0	166.1
	24.0	1.0	105.0	20.0	13.0	502.0	187.1
	24.0	1.0	50.0	12.0	7.0	618.0	165.7
	24.0	1.0	45.0	11.0	9.0	321.0	200.8
AVERAGE CACT=		234.57	AVERAGE CCAL=		159.15		
3	24.0	1.0	10.0	0.0	8.0	119.0	204.9
	24.0	1.0	145.0	10.0	13.0	61.0	182.9
	24.0	1.0	0.0	23.0	9.0	48.0	183.0
	24.0	1.0	20.0	17.0	6.0	91.5	151.8
	24.0	1.0	20.0	13.0	4.0	45.5	136.4
	24.0	1.0	80.0	10.0	6.0	54.4	141.6
	24.0	1.0	10.0	10.0	3.0	200.0	133.7
	24.0	1.0	5.0	15.0	3.0	119.0	123.2
	24.0	1.0	50.0	17.0	11.0	169.0	246.7
	24.0	1.0	10.0	16.0	7.0	129.0	168.1
	24.0	1.0	20.0	12.0	11.0	139.0	242.8
	24.0	1.0	170.0	9.0	10.0	31.5	140.1
3	24.0	1.0	95.0	8.0	15.0	144.0	280.8
	24.0	1.0	75.0	13.0	18.0	166.0	347.0
	24.0	1.0	5.0	20.0	11.0	169.0	220.6
	24.0	1.0	95.0	11.0	13.0	136.0	224.6
	24.0	1.0	90.0	11.0	11.0	148.0	137.0
	24.0	1.0	35.0	14.0	6.0	187.0	144.5
	24.0	1.0	20.0	12.0	9.0	136.0	207.5
	24.0	1.0	35.0	15.0	13.0	1737.0	263.8
	24.0	1.0	160.0	12.0	7.0	12.4	104.7
	24.0	1.0	65.0	11.0	9.0	123.0	187.8
AVERAGE CACT=		189.60	AVERAGE CCAL=		192.43		
4	24.0	1.0	70.0	9.0	8.0	136.0	177.4
	24.0	1.0	135.0	10.0	13.0	69.0	190.0
	24.0	1.0	80.0	23.0	6.0	5.7	150.3
	24.0	1.0	100.0	17.0	6.0	26.4	114.6
	24.0	1.0	100.0	13.0	4.0	29.7	103.4
	24.0	1.0	160.0	10.0	6.0	19.0	100.9
	24.0	1.0	90.0	10.0	3.0	30.2	105.0
	24.0	1.0	35.0	15.0	3.0	23.5	99.2
	24.0	1.0	80.0	25.0	7.0	42.4	124.8
	24.0	1.0	30.0	17.0	13.0	325.0	259.6
	24.0	1.0	60.0	16.0	7.0	105.0	132.7
	24.0	1.0	110.0	12.0	11.0	105.0	219.9
4	24.0	1.0	110.0	9.0	10.0	14.3	172.9
	24.0	1.0	15.0	8.0	15.0	309.0	360.6
	24.0	1.0	15.0	13.0	13.0	452.0	411.5
	24.0	1.0	75.0	20.0	11.0	404.0	185.4
	24.0	1.0	175.0	11.0	13.0	253.0	167.7
	24.0	1.0	10.0	11.0	11.0	256.0	249.3
	24.0	1.0	10.0	11.0	6.0	39.0	140.8
	24.0	1.0	60.0	12.0	9.0	114.0	187.9
	24.0	1.0	45.0	15.0	13.0	272.0	257.2
	24.0	1.0	85.0	20.0	13.0	112.0	206.8
	24.0	1.0	120.0	12.0	7.0	14.5	121.6
	24.0	1.0	145.0	11.0	9.0	90.2	130.8
AVERAGE CACT=		137.27	AVERAGE CCAL=		182.11		
5	24.0	75.0	10.0	9.0	8.0	26.1	25.2
	24.0	75.0	170.0	10.0	13.0	3.0	19.5
	24.0	75.0	20.0	23.0	0.0	48.0	33.1
	24.0	75.0	40.0	17.0	6.0	14.9	22.6
	24.0	75.0	40.0	13.0	4.0	13.6	19.7
	24.0	75.0	100.0	10.0	6.0	22.1	15.5
	24.0	75.0	30.0	15.0	3.0	39.2	17.0
	24.0	75.0	30.0	15.0	3.0	17.6	18.9
	24.0	75.0	20.0	20.0	7.0	32.5	28.6
	24.0	75.0	20.0	17.0	13.0	24.3	43.0
	24.0	75.0	20.0	11.0	7.0	16.0	25.6
	24.0	75.0	20.0	11.0	7.0	16.0	25.6

Table 3.1. (continued)

5	24.0	75.0	5.0	12.0	11.0	5.8	35.1
5	24.0	75.0	165.0	9.0	10.0	2.4	17.6
5	24.0	75.0	70.0	8.0	15.0	10.4	37.5
5	24.0	75.0	50.0	13.0	15.0	2.5	51.0
5	24.0	75.0	20.0	20.0	11.0	7.5	38.6
5	24.0	75.0	120.0	11.0	13.0	39.8	22.6
5	24.0	75.0	65.0	11.0	11.0	7.6	28.5
5	24.0	75.0	10.0	10.0	6.0	43.9	26.6
5	24.0	75.0	5.0	12.0	9.0	13.7	30.1
5	24.0	75.0	10.0	15.0	15.0	19.9	43.3
5	24.0	75.0	30.0	20.0	13.0	18.6	43.1
5	24.0	75.0	175.0	12.0	7.0	1.6	0.7
5	24.0	75.0	90.0	11.0	9.0	12.2	20.9
AVERAGE CACT= 13.88 AVERAGE CCAL= 28.09							
6	24.0	270.0	15.0	9.0	8.0	3.3	4.1
6	24.0	270.0	170.0	10.0	13.0	2.0	3.2
6	24.0	270.0	28.0	24.0	0.0	4.2	6.2
6	24.0	270.0	45.0	17.0	6.0	1.0	4.1
6	24.0	270.0	45.0	13.0	4.0	1.4	3.4
6	24.0	270.0	105.0	10.0	6.0	1.5	2.7
6	24.0	270.0	25.0	26.0	7.0	1.6	5.6
6	24.0	270.0	35.0	17.0	13.0	3.0	7.4
6	24.0	270.0	35.0	10.0	7.0	0.5	4.6
6	24.0	270.0	5.0	12.0	11.0	3.3	5.8
6	24.0	270.0	165.0	9.0	10.0	0.2	3.0
6	24.0	270.0	70.0	8.0	15.0	5.6	5.7
6	24.0	270.0	20.0	20.0	11.0	3.2	7.0
6	24.0	270.0	120.0	11.0	13.0	7.9	3.6
6	24.0	270.0	65.0	11.0	11.0	3.8	4.4
6	24.0	270.0	10.0	19.0	6.0	5.0	5.0
6	24.0	270.0	5.0	12.0	9.0	2.3	5.0
6	24.0	270.0	10.0	15.0	13.0	1.4	7.4
6	24.0	270.0	30.0	20.0	13.0	5.9	7.6
6	24.0	270.0	175.0	12.0	7.0	0.6	1.8
6	24.0	270.0	90.0	11.0	9.0	2.1	3.5
AVERAGE CACT= 2.35 AVERAGE CCAL= 4.82							
7	24.0	350.0	28.0	9.0	8.0	2.0	2.8
7	24.0	350.0	127.0	10.0	13.0	0.4	2.6
7	24.0	350.0	18.0	23.0	9.0	1.8	4.5
7	24.0	350.0	2.0	17.0	6.0	2.0	3.4
7	24.0	350.0	2.0	13.0	4.0	1.3	2.7
7	24.0	350.0	62.0	10.0	6.0	1.1	2.4
7	24.0	350.0	8.0	10.0	3.0	3.6	2.2
7	24.0	350.0	13.0	15.0	3.0	1.3	2.6
7	24.0	350.0	18.0	26.0	7.0	0.2	4.1
7	24.0	350.0	68.0	17.0	13.0	0.7	3.5
7	24.0	350.0	8.0	16.0	7.0	0.1	3.5
7	24.0	350.0	36.0	12.0	11.0	0.1	3.7
7	24.0	350.0	152.0	9.0	10.0	0.4	2.2
7	24.0	350.0	117.0	8.0	16.0	1.0	1.6
7	24.0	350.0	93.0	13.0	18.0	2.6	3.9
7	24.0	350.0	23.0	20.0	11.0	1.0	4.8
7	24.0	350.0	77.0	11.0	13.0	4.5	3.4
7	24.0	350.0	108.0	11.0	11.0	0.2	2.5
7	24.0	350.0	53.0	19.0	6.0	1.7	2.7
7	24.0	350.0	38.0	12.0	9.0	0.6	3.3
7	24.0	350.0	53.0	15.0	13.0	0.9	4.1
7	24.0	350.0	13.0	20.0	13.0	0.6	5.7
7	24.0	350.0	142.0	12.0	7.0	0.8	1.5
7	24.0	350.0	47.0	11.0	9.0	1.0	3.1
AVERAGE CACT= 1.26 AVERAGE CCAL= 3.28							
8	24.0	570.0	105.0	9.0	8.0	0.9	1.4
8	24.0	570.0	50.0	10.0	13.0	1.0	2.0
8	24.0	570.0	95.0	23.0	9.0	0.4	1.0
8	24.0	570.0	75.0	17.0	6.0	0.5	1.3
8	24.0	570.0	75.0	13.0	4.0	0.6	1.3
8	24.0	570.0	15.0	10.0	6.0	1.6	1.5
8	24.0	570.0	145.0	17.0	12.0	0.3	0.9
8	24.0	570.0	18.0	18.0	7.0	1.3	1.3
8	24.0	570.0	115.0	12.0	11.0	0.2	1.3
8	24.0	570.0	75.0	9.0	10.0	2.2	1.6
8	24.0	570.0	170.0	8.0	15.0	1.8	1.8
8	24.0	570.0	170.0	13.0	18.0	0.6	1.2
8	24.0	570.0	100.0	20.0	11.0	0.8	1.1
8	24.0	570.0	0.0	11.0	13.0	2.8	2.2
8	24.0	570.0	175.0	11.0	11.0	0.4	1.2
8	24.0	570.0	130.0	19.0	6.0	0.6	0.9
8	24.0	570.0	115.0	12.0	9.0	0.6	1.3
8	24.0	570.0	130.0	15.0	13.0	0.4	1.1
8	24.0	570.0	90.0	20.0	13.0	0.4	1.4
8	24.0	570.0	65.0	12.0	7.0	0.8	1.5
8	24.0	570.0	30.0	11.0	9.0	0.9	1.8
AVERAGE CACT= 0.87 AVERAGE CCAL= 1.38							
9	24.0	240.0	175.0	9.0	6.0	1.3	3.1
9	24.0	240.0	30.0	10.0	13.0	12.0	7.0
9	24.0	240.0	175.0	23.0	9.0	0.7	0.8
9	24.0	240.0	155.0	17.0	6.0	0.5	1.2
9	24.0	240.0	155.0	13.0	4.0	1.1	1.6
9	24.0	240.0	95.0	10.0	6.0	4.0	3.4
9	24.0	240.0	155.0	10.0	3.0	0.8	2.1
9	24.0	240.0	170.0	15.0	3.0	0.9	1.2
9	24.0	240.0	135.0	17.0	15.0	0.2	2.1
9	24.0	240.0	165.0	15.0	7.0	0.5	1.3
9	24.0	240.0	165.0	12.0	11.0	0.8	2.5
9	24.0	240.0	5.0	9.0	10.0	15.4	5.6
9	24.0	240.0	0.0	8.0	16.0	2.4	6.5
9	24.0	240.0	110.0	13.0	18.0	2.4	5.7
9	24.0	240.0	180.0	20.0	11.0	0.3	1.0
9	24.0	240.0	80.0	11.0	13.0	9.3	5.7
9	24.0	240.0	45.0	11.0	11.0	0.8	4.6
9	24.0	240.0	150.0	19.0	6.0	0.2	1.1
9	24.0	240.0	165.0	12.0	9.0	5.3	2.3
9	24.0	240.0	150.0	15.0	13.0	0.4	2.1
9	24.0	240.0	170.0	23.0	13.0	0.1	1.1
9	24.0	240.0	15.0	12.0	7.0	14.3	5.2
9	24.0	240.0	110.0	11.0	9.0	9.0	3.6
AVERAGE CACT= 3.60 AVERAGE CCAL= 3.07							

Table 3.1. (continued)

10	24.0	1000.0	135.0	9.0	8.0	1.6	0.9
10	24.0	1000.0	20.0	10.0	13.0	1.0	1.2
10	24.0	1000.0	125.0	23.0	9.0	0.6	0.8
10	24.0	1000.0	105.0	17.0	5.0	0.7	0.8
10	24.0	1000.0	125.0	13.0	4.0	0.8	0.9
10	24.0	1000.0	125.0	26.0	7.0	0.5	0.8
10	24.0	1000.0	175.0	17.0	13.0	0.2	0.8
10	24.0	1000.0	115.0	10.0	7.0	0.4	0.8
10	24.0	1000.0	145.0	12.0	11.0	1.0	0.9
10	24.0	1000.0	45.0	9.0	10.0	1.6	1.1
10	24.0	1000.0	140.0	8.0	15.0	2.5	1.1
10	24.0	1000.0	120.0	13.0	18.0	1.5	0.9
10	24.0	1000.0	130.0	20.0	11.0	1.3	0.8
10	24.0	1000.0	30.0	11.0	13.0	2.7	1.2
10	24.0	1000.0	145.0	11.0	11.0	0.8	0.9
10	24.0	1000.0	170.0	19.0	6.0	0.6	0.8
10	24.0	1000.0	145.0	12.0	6.0	0.5	0.8
10	24.0	1000.0	160.0	15.0	13.0	1.6	0.8
10	24.0	1000.0	120.0	20.0	13.0	1.2	0.8
10	24.0	1000.0	35.0	12.0	7.0	1.7	1.1
10	24.0	1000.0	40.0	11.0	9.0	1.3	1.1
AVERAGE CACT=		1.16	AVERAGE CCAL=		0.92		
11	24.0	1250.0	160.0	9.0	8.0	0.6	0.9
11	24.0	1250.0	5.0	10.0	13.0	1.5	1.1
11	24.0	1250.0	150.0	23.0	9.0	0.5	0.8
11	24.0	1250.0	150.0	17.0	6.0	0.7	0.8
11	24.0	1250.0	130.0	13.0	4.0	0.8	0.8
11	24.0	1250.0	70.0	10.0	6.0	1.4	0.9
11	24.0	1250.0	150.0	20.0	7.0	0.2	0.8
11	24.0	1250.0	160.0	17.0	17.0	0.3	0.8
11	24.0	1250.0	140.0	16.0	7.0	0.4	0.8
11	24.0	1250.0	170.0	12.0	11.0	0.5	0.8
11	24.0	1250.0	20.0	9.0	10.0	1.9	1.0
11	24.0	1250.0	115.0	8.0	15.0	1.8	1.0
11	24.0	1250.0	175.0	13.0	18.0	1.6	0.9
11	24.0	1250.0	155.0	20.0	11.0	0.8	0.8
11	24.0	1250.0	55.0	11.0	13.0	2.7	1.0
11	24.0	1250.0	120.0	12.0	11.0	1.1	0.9
11	24.0	1250.0	170.0	12.0	9.0	0.9	0.8
11	24.0	1250.0	175.0	15.0	13.0	1.4	0.8
11	24.0	1250.0	145.0	20.0	13.0	0.6	0.8
11	24.0	1250.0	10.0	12.0	7.0	1.0	1.0
11	24.0	1250.0	65.0	11.0	9.0	1.3	0.9
AVERAGE CACT=		1.09	AVERAGE CCAL=		0.86		
12	24.0	1750.0	150.0	9.0	8.0	0.5	0.8
12	24.0	1750.0	5.0	10.0	13.0	0.3	0.9
12	24.0	1750.0	140.0	33.0	6.0	0.5	0.8
12	24.0	1750.0	120.0	17.0	6.0	0.7	0.8
12	24.0	1750.0	120.0	13.0	4.0	0.8	0.8
12	24.0	1750.0	60.0	10.0	6.0	1.4	0.8
12	24.0	1750.0	130.0	13.0	3.0	0.8	0.8
12	24.0	1750.0	135.0	15.0	3.0	1.0	0.8
12	24.0	1750.0	170.0	17.0	13.0	0.2	0.8
12	24.0	1750.0	130.0	16.0	7.0	0.2	0.8
12	24.0	1750.0	160.0	12.0	11.0	0.3	0.8
12	24.0	1750.0	30.0	9.0	10.0	1.6	0.9
12	24.0	1750.0	125.0	8.0	15.0	1.2	0.9
12	24.0	1750.0	145.0	13.0	18.0	4.0	0.8
12	24.0	1750.0	145.0	30.0	11.0	0.5	0.8
12	24.0	1750.0	45.0	11.0	13.0	0.7	0.9
12	24.0	1750.0	130.0	11.0	11.0	0.2	0.8
12	24.0	1750.0	175.0	19.0	6.0	0.1	0.8
12	24.0	1750.0	160.0	12.0	4.0	0.5	0.8
12	24.0	1750.0	175.0	15.0	13.0	0.9	0.8
12	24.0	1750.0	135.0	20.0	13.0	0.4	0.8
12	24.0	1750.0	20.0	12.0	7.0	1.2	0.9
12	24.0	1750.0	75.0	11.0	9.0	0.7	0.8
AVERAGE CACT=		0.81	AVERAGE CCAL=		0.81		
13	24.0	65.0	120.0	9.0	8.0	2.0	21.0
13	24.0	65.0	110.0	23.0	9.0	1.0	14.2
13	24.0	65.0	90.0	17.0	6.0	0.8	17.6
13	24.0	65.0	60.0	13.0	4.0	0.6	16.2
13	24.0	65.0	30.0	10.0	6.0	2.4	25.9
13	24.0	65.0	100.0	10.0	3.0	1.7	15.0
13	24.0	65.0	105.0	15.0	3.0	1.1	12.2
13	24.0	65.0	140.0	12.0	17.0	0.3	11.0
13	24.0	65.0	100.0	10.0	7.0	0.2	17.2
13	24.0	65.0	130.0	12.0	11.0	4.0	20.3
13	24.0	65.0	60.0	9.0	10.0	37.2	31.9
13	24.0	65.0	165.0	3.0	15.0	4.2	34.7
13	24.0	65.0	175.0	13.0	18.0	3.0	23.8
13	24.0	65.0	115.0	20.0	11.0	0.4	16.6
13	24.0	65.0	15.0	11.0	13.0	15.5	46.9
13	24.0	65.0	140.0	11.0	11.0	1.1	18.5
13	24.0	65.0	130.0	12.0	9.0	3.2	17.4
13	24.0	65.0	145.0	15.0	13.0	1.7	16.3
13	24.0	65.0	105.0	20.0	13.0	12.8	22.7
13	24.0	65.0	60.0	12.0	7.0	17.4	27.1
13	24.0	65.0	45.0	11.0	9.0	4.8	31.9
AVERAGE CACT=		5.61	AVERAGE CCAL=		21.88		
							AVERAGE CR= 3.773364
14	24.0	165.0	155.0	9.0	8.0	0.4	5.3
14	24.0	165.0	165.0	23.0	9.0	1.0	1.1
14	24.0	165.0	175.0	17.0	6.0	1.0	1.6
14	24.0	165.0	175.0	13.0	4.0	0.5	2.3
14	24.0	165.0	115.0	10.0	6.0	13.1	5.0
14	24.0	165.0	175.0	10.0	3.0	0.9	3.3
14	24.0	165.0	170.0	15.0	3.0	0.8	1.8
14	24.0	165.0	175.0	16.0	7.0	1.0	1.9
14	24.0	165.0	145.0	12.0	11.0	0.9	4.8
14	24.0	165.0	25.0	9.0	10.0	27.0	9.6
14	24.0	165.0	70.0	8.0	16.0	4.0	12.2
14	24.0	165.0	90.0	13.0	18.0	1.6	12.7
14	24.0	165.0	160.0	20.0	11.0	0.4	1.6
14	24.0	165.0	100.0	11.0	13.0	19.5	8.6
14	24.0	165.0	75.0	11.0	11.0	1.6	9.0
14	24.0	165.0	145.0	12.0	9.0	3.4	4.2
14	24.0	165.0	130.0	15.0	13.0	0.7	4.7
14	24.0	165.0	170.0	20.0	13.0	1.1	1.6
14	24.0	165.0	25.0	12.0	7.0	21.3	8.4
14	24.0	165.0	130.0	11.0	9.0	7.7	5.2
AVERAGE CACT=		5.43	AVERAGE CCAL=		9.24		

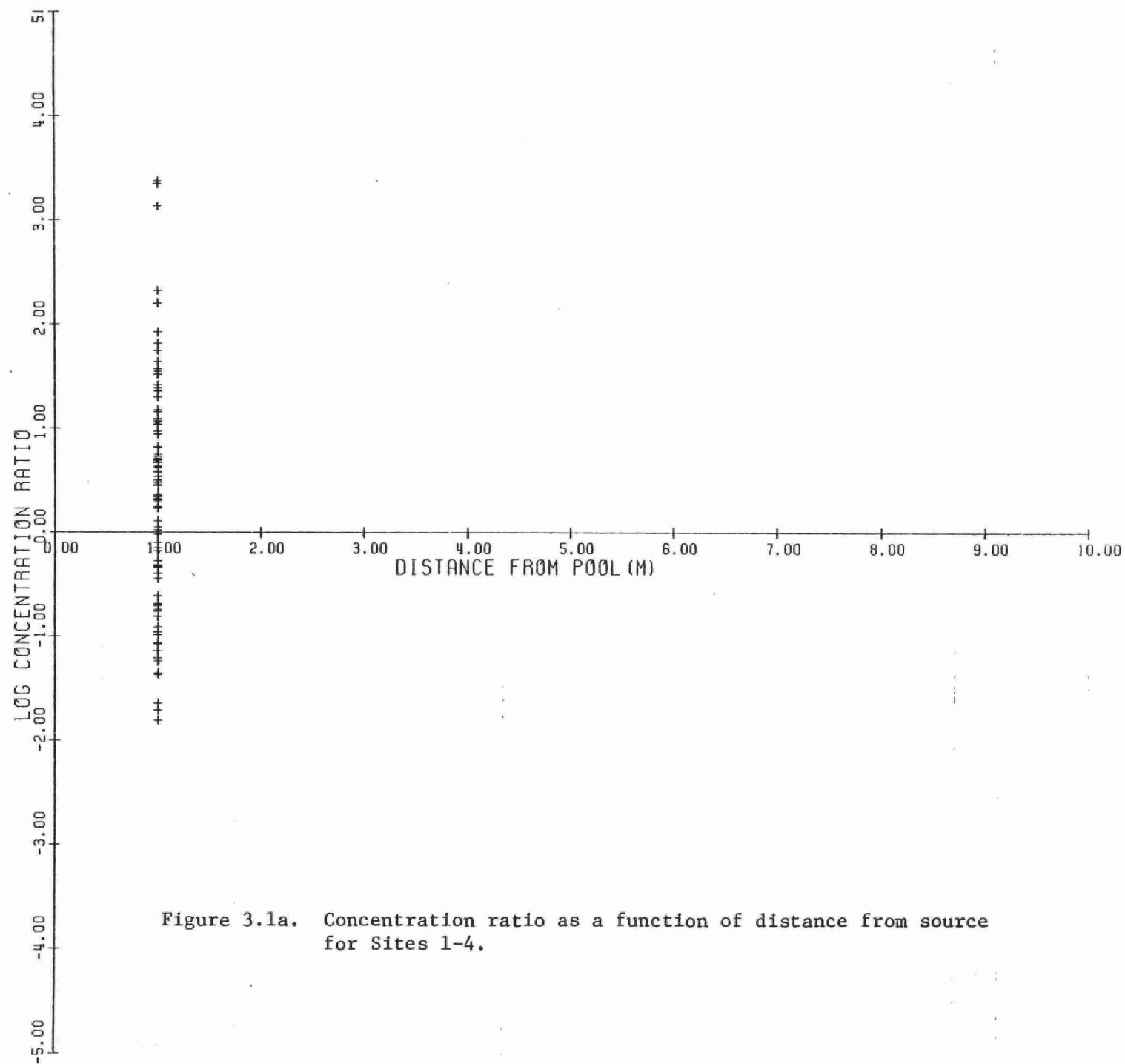


Figure 3.1a. Concentration ratio as a function of distance from source for Sites 1-4.

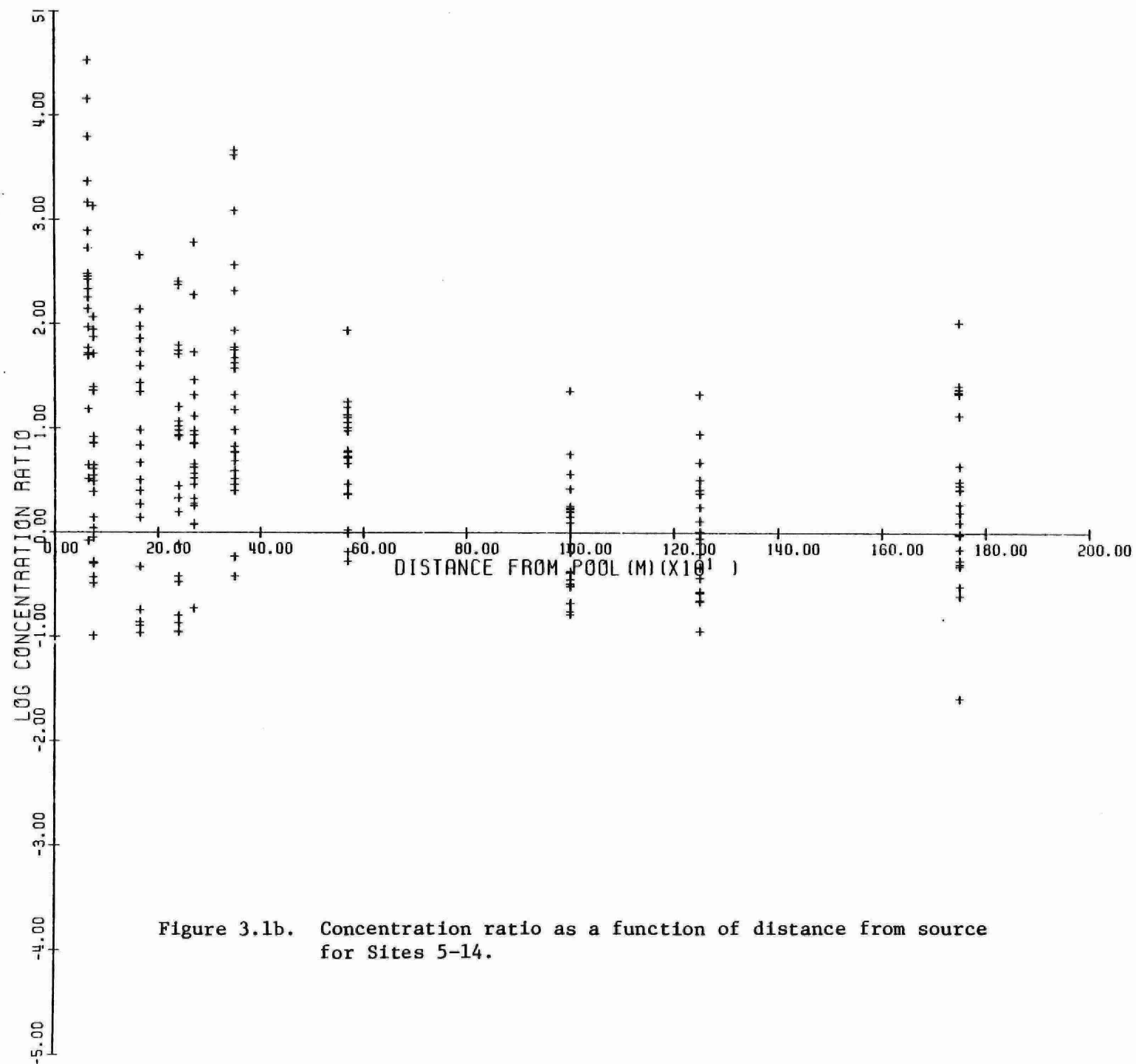


Figure 3.1b. Concentration ratio as a function of distance from source for Sites 5-14.

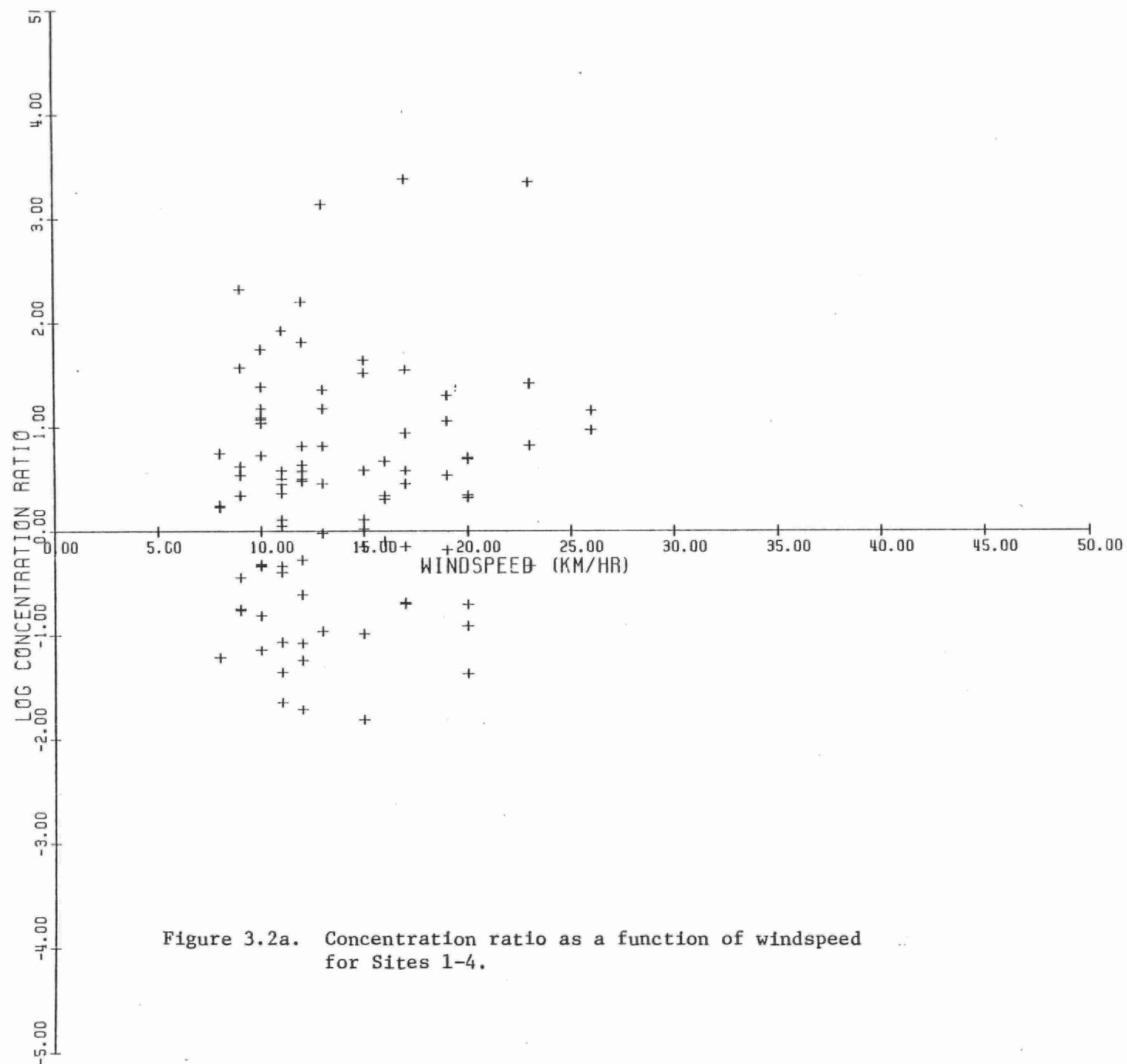


Figure 3.2a. Concentration ratio as a function of windspeed for Sites 1-4.

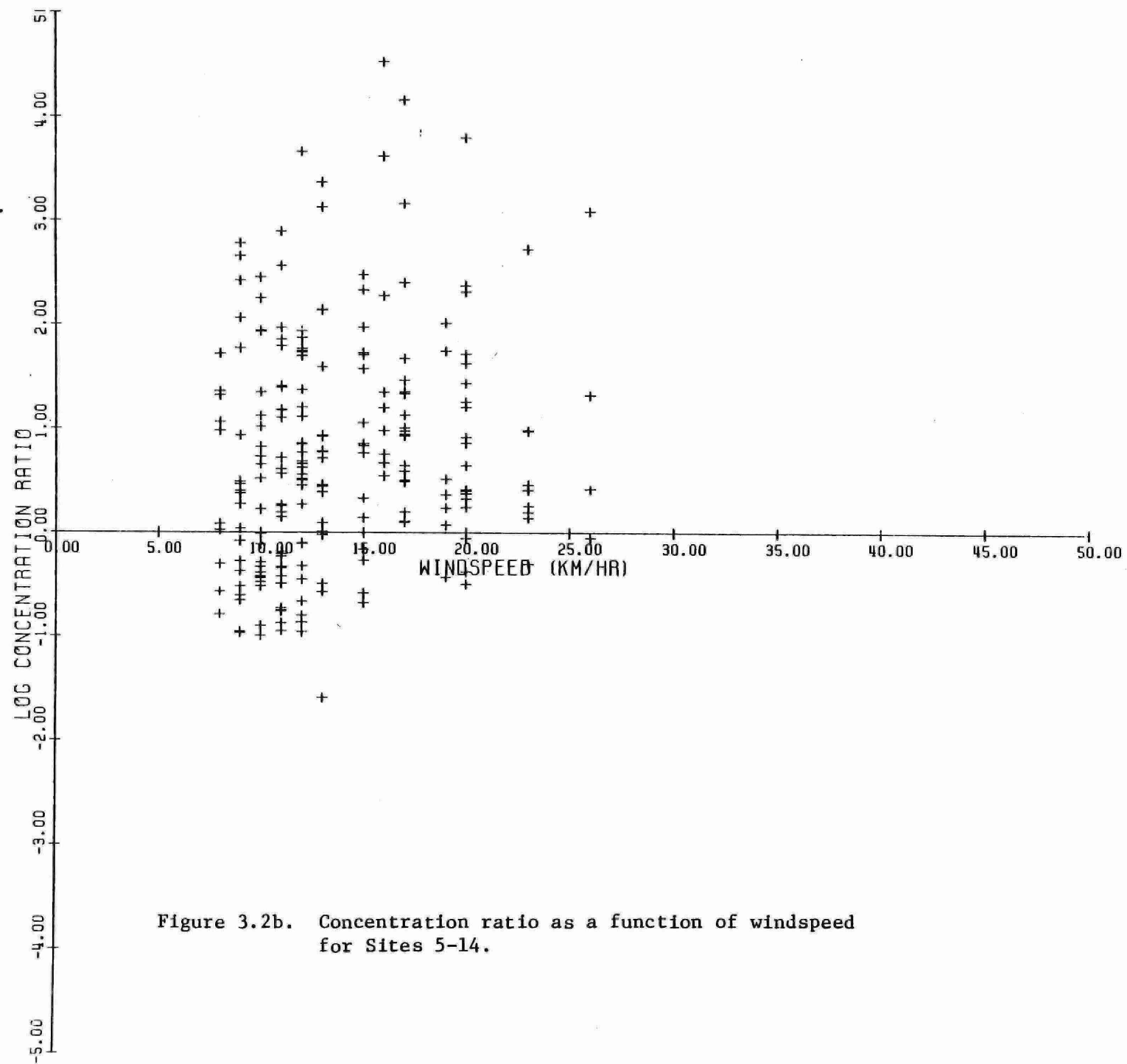


Figure 3.2b. Concentration ratio as a function of windspeed for Sites 5-14.

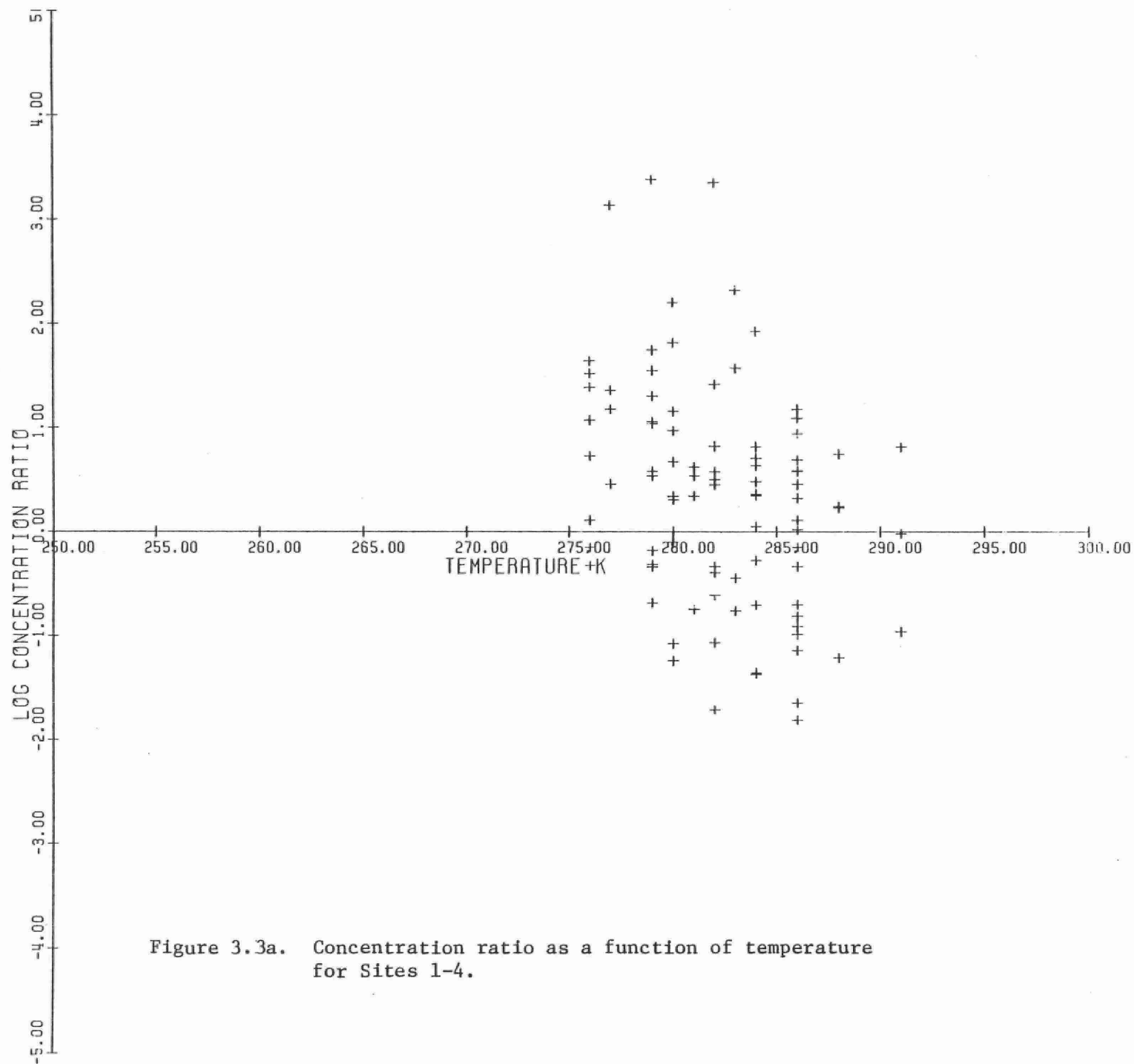
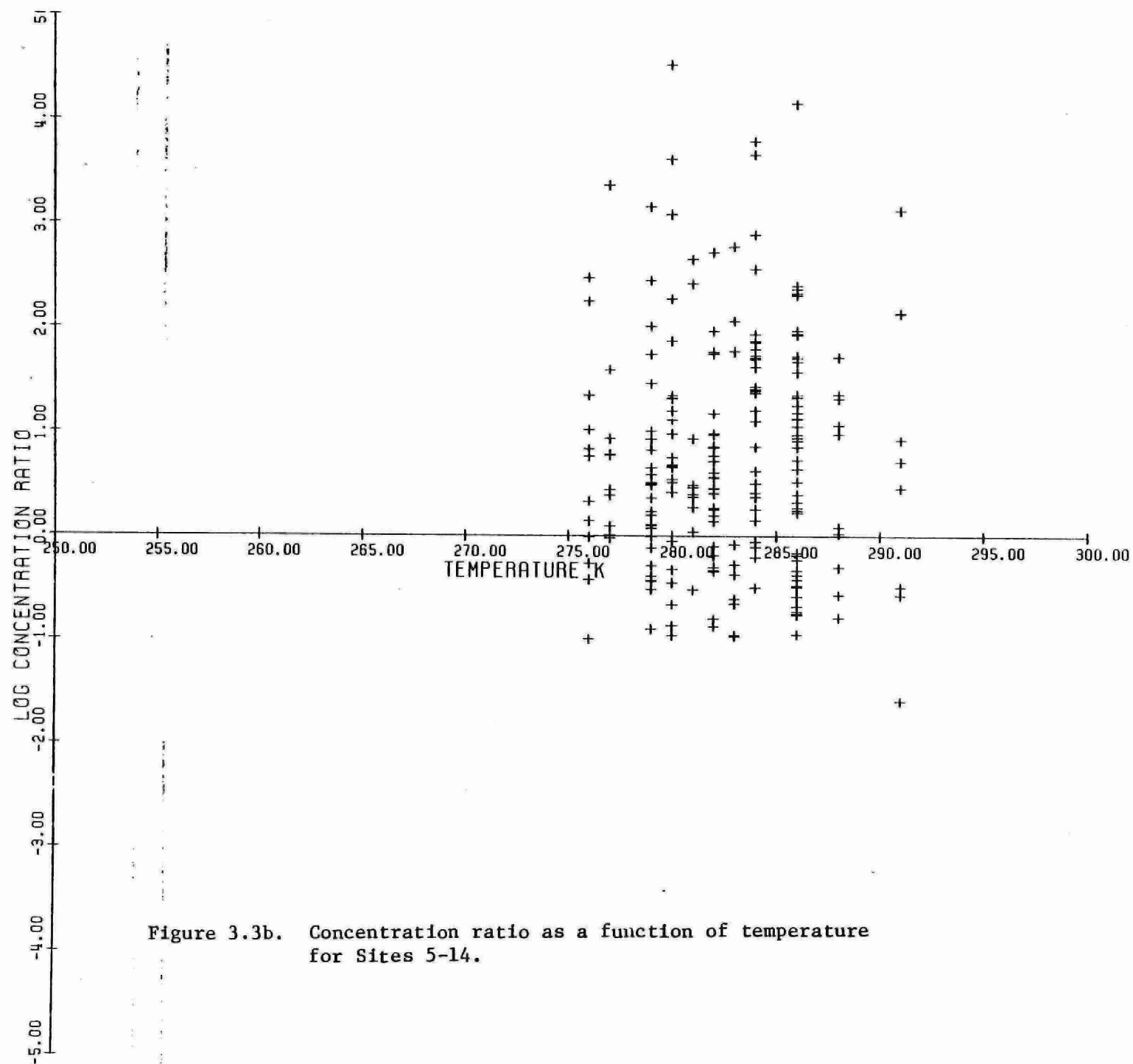


Figure 3.3a. Concentration ratio as a function of temperature for Sites 1-4.



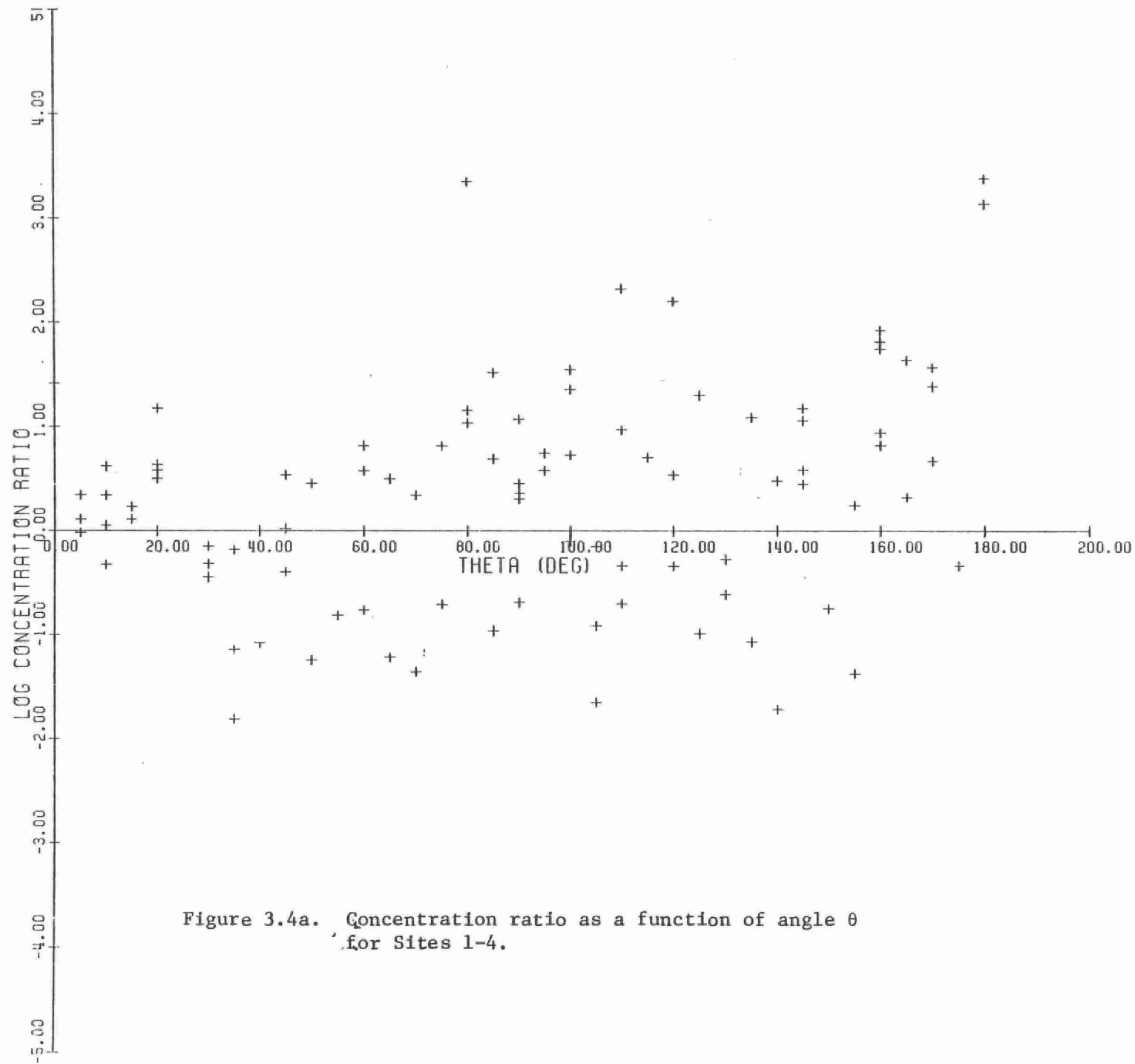


Figure 3.4a. Concentration ratio as a function of angle θ for Sites 1-4.

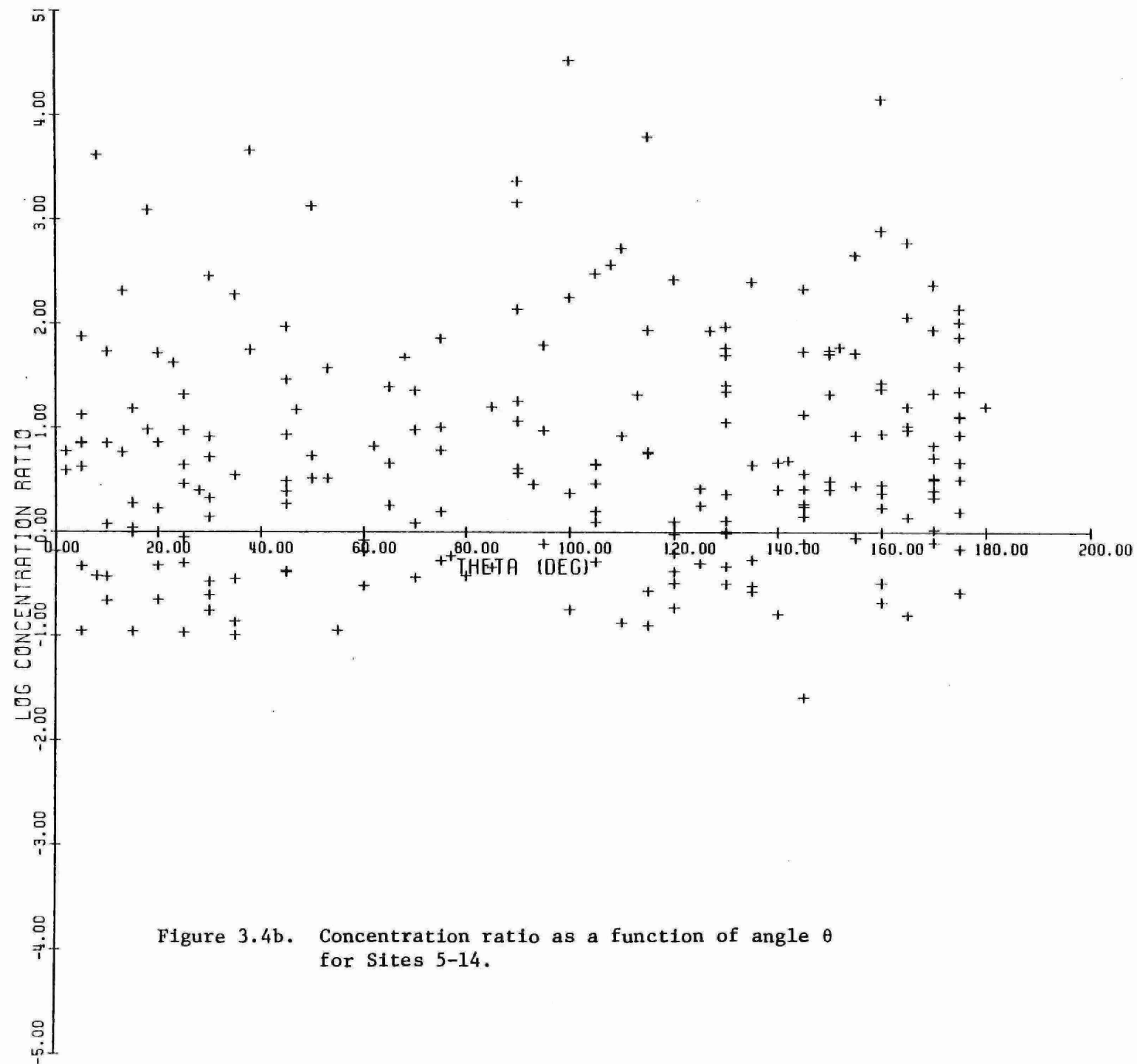


Figure 3.4b. Concentration ratio as a function of angle θ for Sites 5-14.

4. APPLICATION TO ISABELLA STREET SCHOOL

On October 8, 1980 a transformer at the Isabella Street School Thunder Bay, Ontario ruptured and spilled approximately 130 litres of fluid containing approximately 70% PCB compounds. The transformer was situated near the east wall of the school at ground level. The spill covered approximately 100 m^2 adjacent to the school and 10 m^2 in patches up to 25 m from the school. The Ministry of the Environment monitored the concentrations in the school yard and building for several days after the spill.

Using prevailing temperature and wind speed; and spill dimensions and sampling time supplied by the Ministry, the calculation procedure described in Appendix I was used to calculate concentrations at various distances from the school. The results are given in Table 4.1.

Concentrations measured indoors at the school are not calculable using this model. A fair estimate would be to assume that indoor and outdoor concentrations were equal, especially if there is rapid air exchange. In the event that the liquid was spilled in part indoors, an entirely different situation would apply.

Table 4.1 Concentrations at Isabella St. School at various distances from the spill

Conditions	Distance from spill edge (m)	Sampling Time (h)	Concentration (ng/m^3)	
			at height 0 m	at height 1 m
$\theta = 0.0^\circ$ $U = 4.2 \text{ m/s}$ (15 km/h) $T = 280 \text{ K}$ $P = 0.0048$ $A = 100 \text{ m}^2$	0	1	4200	560
	3	1	2300	1500
	10	1	830	730
	20	1	402	370
	23	24	140	140
	100	1	39	39

The results show that concentrations of 1500 to 2300 ng/m³ are predicted at a distance 3 m from the spill edge at heights of 0 and 1 m. These values are higher than those obtained experimentally by about a factor of two. At 10 m distance, the concentrations of 730 to 830 ng/m³ are close to those obtained experimentally. By 20 m the concentrations have fallen below 500 ng/m³ for short sampling times (1 hour) - which is the worst case. The long (24 hour) sampling time values are a factor of approximately 3 lower. By 100 m distance, levels of 39 ng/m³ are expected, well below any level of concern.

It must be emphasised that the air flow characteristics in this region may be quite abnormal due to channelling between buildings, and flow over and around buildings. It appears that these flow "abnormalities" cause an increase in σ_z in the region of the spill, i.e. vertical mixing is quite rapid. It is probably impossible to quantify such flows accurately; thus the only approach appears to be to use the calculation procedure as a pessimistic estimate and interpret the results in a toxic sense with an awareness that the concentrations may be overestimates by factors of up to 5. There may be periodic air gusts with very high concentrations even as large as 13,000 ng/m³ (the value over the pool) but with others containing negligible PCB.

In general, this test of the equation is taken as being satisfactory in that the calculated concentrations are within factors of 2 of those observed. It is puzzling, however, that some very much higher concentrations were not obtained close to the transformer.

5. DISCUSSION AND CONCLUSIONS

A calculation procedure has been developed and illustrated in which air concentrations can be calculated in the vicinity of spills of evaporating liquids. It is emphasised that the contribution here is to bring together the component processes into an overall package which it is believed will be useful to the on-scene response team. There are several areas of improvement possible as follows.

1. The vapour pressure estimation from boiling point applies only for non-polar organics. A listing of vapour pressures at various temperatures for "candidate" substances would be valuable.
2. The evaporation mass transfer coefficient depends on pool size and on the evaporating substance. A better correlation is possible.
3. The values of σ_y and σ_z depend on atmospheric state and should thus be taken as "typical values". Under stable conditions when the plume is more confined the procedure will underestimate concentrations at ground level on the centreline. Some judgement is thus necessary when selecting values under stable conditions. For example, at night under a clear sky, σ_y and σ_z may be lower by a factor of 2 or 3.
4. The pool temperature may be higher or lower than ambient depending on radiation and evaporative cooling. Again, judgement is necessary.
5. This analysis does not apply to plumes which are sufficiently concentrated that they have positive or negative buoyancy. Of particular concern, are dense plumes (i.e. cold or with high concentrations of high molecular weight gas) which will spread over the ground at high concentration.

6. There is no doubt that sampling time enters the calculation but the equation presented has little justification. A better equation should be devised.

7. The vertical coefficient σ_z is influenced by terrain "roughness", probably increasing by approximately the magnitude of the size of the object. Again, judgement is necessary. There is a danger, however, that overestimating it will lead to underestimation of concentration - which is unsafe. The safest procedure is to underestimate σ_z .

In summary, it is believed that the procedure developed has sufficient rigour that the results are credible, but the concentrations must be regarded as estimates. Several improvements are possible and could be explored. It is recommended that the procedure be tested in the field to gain an appreciation of its applicability. Is it too complex or insufficiently complex? Such experience would be valuable as a guide for future work. The procedure also highlights the monitoring data which could be taken at spill sites which could be used to "validate" the procedure. Such data (and those discussed here) are an invaluable source of information about spill evaporation and dispersion and it is hoped that they can be exploited, as has been attempted here, in the interests of providing better response advice following accidental spills.

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APPENDIX I

```

FORTRAN IV G1 RELEASE 2.0          MAIN          DATE = 82067          12/17/56          PAGE 0001

0001      DIMENSION SD(400),X(400),WD(400),WSKH(400),CACT(400),CCAL(400),TC(
0002      *AD(400),CPL(400),SDIR(400),WDIR(400)
0003      DIMENSION SIGZ(400),SIGTH(400),Q(400),D(400),E(400),F(400),G(400),
0004      *CC(400),H(400),NN(400)
0005      DIMENSION WSMS(400),VP(400),CSAT(400),SIGP(400),TK(400)
0006      DIMENSION CRL(400),CPLA(400),DC(400),CRLI(400)
0007      DIMENSION XARRAY(4),YARRAY(4)
0008      DIMENSION XX(400),TKK(400),WSKH(400)
0009      DIMENSION SSDIR(400)
0010      C1=0.15
0011      C2=5.0
0012      C3=0.05
0013      C4=1.0
0014      JL=1
0015      ARS=7000.
0016      ARAT=25.
0017      ARP=ARS/ARAT
0018      DIA=(4.0*ARS/3.1416)**0.5
0019      TB=350.0
0020      TBK=TB+273.0
0021      WD25=2.0*1E-02
0022      CBACK=0.75
0023      P=8.314
0024      WM=292.0
0025      Z=0.0
0026      SCR=0.0
0027      N=312
0028      DU 10 I=1,N
0029      LEAD(5,100)NN(I),CQ(I),X(I),SDIR(I),WDIR(I),WSKH(I),CACT(I),TC(I)
0030      100 FORMAT(12,4X,F6.1,2X,3F6.1,1X,F4.1,1X,F6.1,2X,F5.1)
0031      IF(X(I).EQ.0.0) X(I)=1.0
0032      IF(NN(I).LE.0) X(I)=1.0
0033      WD(I)=ABS(CQIR(I)-WDIR(I))
0034      IF(WD(I).GT.180.0) WD(I)=ABS(WD(I)-360.0)
0035      WSMS(I)=WSKH(I)/3.0
0036      TK(I)=TC(I)+273.0
0037      VP(I)=VP25*EXP(10.6*TK(I)-0.298*0-1.0/TK(I))
0038      CE=0.002*WSMS(I)**0.78
0039      SIGZ(I)=C3*OIA+C1*X(I)
0040      SIGP(I)=DIA+C4+C2*X(I)/WSMS(I)
0041      SIGTH(I)=SIGP(I)*180./((3.1416*(X(I)+DIA*0.5))
0042      IF(SIGTH(I).GT.180.0) SIGP(I)=3.1416*(X(I)+DIA*0.5)
0043      IF(SIGTH(I).GT.180.0) SIGTH(I)=180.0
0044      Q(I)=CE*AMP*VP(I)*WM*1E09/(R*TK(I))
0045      E(I)=1.0/(1.1416*WSKH(I)*SIGZ(I)*SIGP(I))
0046      F(I)=EXP(-(Z**2)/(2.0*SIGZ(I)**2))
0047      G(I)=EXP(-(WD(I)-360)**2/(2*SIGTH(I)**2))
0048      H(I)=F(I)*G(I)
0049      CCAL(I)=Q(I)*D(I)*E(I)*H(I)+CBACK
0050      CR(I)=CCAL(I)/CACT(I)
0051      CRL(I)=ALDG(CR(I))
0052      CRLA(I)=ABS(CRL(I))
0053      CR(I)=ABS(CCAL(I)/CACT(I))
0054      CSAT(I)=VP(I)*WM*1E09/(R*TK(I))+CBACK
0055      CO(I)=Q(I)/(WSMS(I)*DIA*DIA*C3)+CBACK
0056      SCR=SCR+CR(I)
0057      10 CONTINUE
0058      DO 20 J=1,14
0059      TCACT=0
0060      TCRL=0.0
0061      TCRLA=0.0
0062      TCCAL=0
0063      DU 30 I=1,312
0064      IF(NN(I).EQ.0) GOTO 40
0065      GOTO 29
0066      40 CONTINUE
0067      TCACT=TCACT+CACT(I)
0068      TCCAL=TCCAL+CCAL(I)
0069      TCRL=TCRL+CRL(I)
0070      TCRLA=TCRLA+CRLA(I)
0071      WDD(JL)=WD(JL)
0072      XX(JL)=X(I)
0073      WWSKH(JL)=WSKH(I)
0074      TKK(JL)=TK(I)
0075      WDD(JL)=WD(I)
0076      SSDIR(JL)=SDIR(I)
0077      CRL(JL)=CRL(I)
0078      JL=JL+1
0079      JL=JL+1
0080      WRITE(6,102)NN(I),SD(I),X(I),WD(I),WSKH(I),TC(I),CACT(I),CCAL(I)
0081      102 FORMAT(' ',12,7F12.1)
0082      20 CONTINUE
0083      30 CONTINUE
0084      JK=JJ-1
0085      AVCACT=TCACT/JK
0086      AVCCAL=TCCAL/JK
0087      AVCRLA=TCRLA/JK
0088      AVCRL=TCRL/JK
0089      WRITE(6,103)AVCACT,AVCCAL
0090      103 FORMAT('0',10,1,AVERAGE CACT=1,F10.2,5X,AVERAGE CCAL=1,F10.2,7,1)
0091      JJ=1
0092      20 CONTINUE
0093      SCR=SCR/N
0094      WRITE(6,105)SCR
0095      105 FORMAT('0',10,1,AVERAGE CR=1,F10.6)
0096      RETURN
0097      END

```

SAMPLE CALCULATION

APPENDIX I

CALCULATION PROCEDURE

1. Environmental conditions

Wind speed $U = 4.2$ m/s (1 km/hr = 0.278 m/s)

Temperature $t_E = 7$ °C $T_E = t_E + 273 = 280$ K

$K_e = 0.0025 U^{0.78} = 0.0076$ m/s

2. Substance Properties

Molecular weight $M = 292$ g/mol

Mole or volume fraction $x = 0.6$ fraction

Density $d = 1.2$ g/cm³

Vapour pressure $P = 0.0048$ Pa (see below)

Note Vapour Pressure (VP)

To convert atm to Pa multiply by 101325

" " mm Hg to Pa " " 133

If VP P_D is available at another temperature t_D °C then estimate the environmental VP P_E at temperature t_E °C from

$$P_E = P_D \exp[10.6(t_B + 273)(1/(t_D + 273) - 1/(t_E + 273))]$$

where t_B is the boiling point °C.

If no VP is available but the boiling point t_B °C is known then

$$P_E \approx 101325 \exp(10.6(1 - (t_B + 273)/(t_E + 273)))$$

3. Spill Properties

Volume spilled $V = 0.132$ m³ Note: 1 m³ = 35.3 ft³
= 220 Igall
= 264 USgall
= 1000 litres
= 6.3 barrels

Area of spill $A = 100$ m²

Depth of spill $D = V/A = 0.0013$ m

Diameter of pool $H = 10$ m

4. Estimate Evaporation Rate Q

Evaporation rate $Q = \frac{K_e A P x H}{RT_E}$ g/s where $R = 8.314$
 $T_E = t_E + 273$
 $= 2.75 \times 10^{-4}$ g/s

Spill lifetime $t = 10^6 V d / Q = 5.87 \times 10^8$ s

Note If spill depth D is known

$$t = 10^6 D d R T / (K_e P x H) = \text{ } s$$

5. Estimate Concentrations in Area of Pool

(i) Maximum concentration at spill surface

$$C_B = P H / R T \text{ g/m}^3 = 6.02 \times 10^{-4} \text{ g/m}^3$$

(ii) Concentration above pool

$$C_p = Q / (0.05 H^2) = 1.29 \times 10^{-5} \text{ g/m}^3$$

6. Estimate Dispersion Coefficients

Desired distance $X = 3$ m

Sampling time $S = 1$ hours

Vertical coefficient $\sigma_z = 0.05H + 0.15X = 0.95$ m

Horizontal coefficient $\sigma_y = H + S^{0.5} X / U = 10.7$ m

Angular coefficient $\sigma_\theta = 180 \sigma_y / (nX) = 204.4$ degrees

(If σ_θ exceeds 180° use 180° and recalculate

σ_y from

$$\sigma_y = nX = 9.42 \text{ m}$$

7. Calculate Centreline Ground Level Concentration at X

$$C_c = Q / (n U \sigma_z \sigma_y) = 2.3 \times 10^{-6} \text{ g/m}^3 = 2300 \text{ ng/m}^3$$

8. Calculate Concentration Off-Ground and Off-Centreline

Height $Z = 1$ m

Angle between wind and subject $\theta = 0$ degrees

Height factor $F_z = \exp(-z^2 / (2\sigma_z^2)) = 0.575$ m

Angle factor $F_\theta = \exp(-\theta^2 / (2\sigma_\theta^2)) + \exp(-(\theta - 360)^2 / (2\sigma_\theta^2))$

$$= 1.135 \text{ degrees}$$

Concentration $C = C_c F_z F_\theta = 1.5 \times 10^{-6} \text{ g/m}^3$

$$= 1500 \text{ ng/m}^3$$

SAMPLE CALCULATION

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Wind speed $U = 4.2$ m/s (1 km/hr = 0.278 m/s)

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" " mm Hg to Pa " " 133

If VP P_D is available at another temperature t_D °C then estimate the environmental VP P_E at temperature t_E °C from

$$P_E = P_D \exp[10.6(t_B + 273)/(1/(t_D + 273) - 1/(t_E + 273))]$$

where t_B is the boiling point °C.

If no VP is available but the boiling point t_B °C is known then

$$P_E \approx 101325 \exp(10.6(1 - (t_B + 273)/(t_E + 273)))$$

3. Spill Properties

Volume spilled $V = 0.132$ m³

Note: 1 m³ = 35.3 ft³
= 220 lgall
= 264 USgall
= 1000 litres
= 6.3 barrels

Area of spill $A = 100$ m²

Depth of spill $D = V/A = 0.0013$ m

Diameter of pool $H = 10$ m

4. Estimate Evaporation Rate Q

Evaporation rate $Q = \frac{K_E A P x M}{RT_E}$ g/s

where $R = 8.314$
 $T_E = t_E + 273$

$$= 2.75 \times 10^{-4} \text{ g/s}$$

Spill lifetime $\tau = 10^6 V d / Q$ s = 5.87×10^8 s

Note If spill depth D is known

$$\tau = 10^6 D A R T / (K_E P x M) \text{ s} = \text{ } \text{ s}$$

5. Estimate Concentrations in Area of Pool

(i) Maximum concentration at spill surface

$$C_B = P H / R T \text{ g/m}^3 = 6.02 \times 10^{-4} \text{ g/m}^3$$

(ii) Concentration above pool

$$C_P = Q / (0.05 H^2) = 1.29 \times 10^{-5} \text{ g/m}^3$$

6. Estimate Dispersion Coefficients

Desired distance $X = 3$ m

Sampling time $S = 1$ hours

Vertical coefficient $\sigma_z = 0.05H + 0.15X = 0.95$ m

Horizontal coefficient $\sigma_y = H + S^{0.5} X / U = 10.7$ m

Angular coefficient $\sigma_\theta = 180 \sigma_y / (\pi X) = 204.4$ degrees

(If σ_θ exceeds 180° use 180° and recalculate

σ_y from

$$\sigma_y = \pi X = 9.42 \text{ m}$$

7. Calculate Centreline Ground Level Concentration at X

$$C_c = Q / (\pi U \sigma_z \sigma_y) = 2.3 \times 10^{-6} \text{ g/m}^3 = 2300 \text{ ng/m}^3$$

8. Calculate Concentration Off-Ground and Off-Centreline

Height $Z = 1$ m

Angle between wind and subject $\theta = 0$ degrees

Height factor $F_z = \exp(-z^2 / (2 \sigma_z^2)) = 0.575$

Angle factor $F_\theta = \exp(-\theta^2 / (2 \sigma_\theta^2)) + \exp(-(\theta - 360)^2 / (2 \sigma_\theta^2))$

$$= 1.135 \text{ degrees}$$

Concentration $C = C_c F_z F_\theta = 1.5 \times 10^{-6} \text{ g/m}^3$

$$= 1500 \text{ ng/m}^3$$



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